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FORMATION OF MESOPOROUS ZSM-5 FROM NATURAL KAOLIN AND COLLOIDAL SILICA WITH TWO-STEP CRYSTALLIZATION

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Abstract

Influence of crystallization step on the formation of mesoporous ZSM-5 was studied. Mesoporous ZSM-5 were directly synthesized using natural kaolin and colloidal silica as a source of silica and alumina, silicalite seed to induce the formation of ZSM-5 and CTABr (cetyltrimethylammonium bromide) as cationic surfactan for meso structure, with molar ratio $10Na_2O$: $100SiO_2$: $2Al_2O_3$: $1800H_2O$, SiO_2 / CTABr = 3.85. Synthesis of mesoporous ZSM-5 was carried out using one-step crystallization at 127,5 °C and two-step crystallization at 80 and 150 °C. The solids formed were then characterized using X-ray diffraction (XRD), infrared spectroscopy (FTIR), N_2 adsorption and scanning electron microscopy-EDX (SEM-EDX) methods. The results showed that diffraction peaks characteristic of ZSM-5 appeared at 2θ = 7-9° and 23-25°. It was shown that the change in crystallization step could influence to the structure, crystallinity and pores of the ZSM-5 materials. Cristallinity of mesoporous ZSM-5 with two-step crystallization was higher than one-step crystallization. FTIR results showed band at around 960 cm^{-1}, attributable to terminal silanol groups on the wall surface of the mesopores. The BJH mesopore area based on the N_2 adsorption was obtained around 882 m^2/gr and 325 m^2/gr for ZSM-5 with two-step and one-step crystallization, respectively.

Keyword: mesoporous ZSM-5, natural kaolin, two-step crystallization

INTRODUCTION

Zeolites are three-dimensional crystalline microporous solids with corner-sharing AlO_4 and SiO_4 tetrahedra forming frameworks that lead to channels and cages in the structures [1]. Traditionally, zeolites are synthesized from sodium silicate and aluminate [2,3]. However, other alumino-silicate rich materials such as kaolin have also been used [4-6]. Kaolin is a natural mineral which is one type of clay which is primarily composed of the mineral kaolinite. Kaolinite is derived from the decomposition of feldspar, as material mixture with other oxides such as calcium oxide, magnesium oxide, potassium oxide, sodium oxide, iron oxide, and others. Kaolin is widely used in the paper industry. In this paper industry serves as a filler pulp where the presence of kaolin in the paper will add weight, more white, not transparent and not easily torn. Highly reactive kaolin phase, metakaolin, was reported to have been produced at 900 °C and used for synthesis of pure phase zeolites [7]. Kaolin can be used as raw material to synthesize zeolites. After the first reported synthesis of zeolite-A from kaolin in 1988 [8], continuous efforts have been made to prepare various types of zeolites, such as zeolite-13X, zeolite-β, and ZSM-5 [9,10], which exhibit good catalytic performance due to more active sites.

ZSM-5 zeolites have been widely used as catalysts and selective sorbents in the petrochemical industry owing to their high thermal stability, intrinsic acidity, high surface area and well-defined porosity [11,12]. The uniform micropore distribution of zeolites is responsible for their high shape selectivity observed in various reactions. However, this feature also leads to diffusion limitations when large molecules diffuse in relatively narrow channels. Some active sites are hindered from contacting reactants due to restricted transport processes [13,14]. As a consequence, it is highly needed to develop new materials with a mesoporous architecture of porosity. Several potential solutions have been proposed to overcome the diffusion limitation imposed by zeolitic structures: synthesizing new zeolites with larger pores, such as synthesizing mesoporous ZSM-5 [15].

One of these attempts is the synthesis of ordered mesoporous ZSM-5 from solutions of zeolite precursors or ‘‘seeding gels’[16-19] in the presence of surfactants as mesostructure directing agents. This method was introduced in 2000 by Liu et al. [16], who described the synthesis of mesoporous aluminosilicates from aged gels known to promote the crystallisation of zeolite-Y [16], ZSM-5 or zeolite-β [17]. To these so called ‘‘seeding gels’’, which are believed to contain precursors of the desired zeolite structure, they added a mesostructure directing surfactant. On the other hand, Huang et al. [18] and more recently Frunz et al. [19] and Goncalves et al. [20] reported the crystallisation of mesoporous ZSM-5 crystals from the respective seeding gel in the presence of a cationic surfactant.

Some of important parameters describing the process of zeolite crystallization like the nucleation and crystallization rates depend on the dissolution of the silica precursors. The fragile silicate intermediates released during the process of the silica dissolution, which play an important role in zeolite formation, are also influenced by the nature of the silica used. Besides the effects on the formation of a particular zeolite, the silica source can influence the specific features of the zeolite material [21]. The impurities introduced by the silica source in the starting system can also affect the morphology [22] and chemical properties [23,24] of the zeolite.

Goncalves et al. [25] and Eimer et al. [26] were synthesized mesoporous ZSM-5 with aging temperature and time variation (60 and 80°C) to formation and crystallization with CTABr template. Petushkov et al. [27] using temperature of 140-165 °C with a time of 12-72 hours and obtain high mesoporous volume. Crysallization time variation and templates are also conducted by Xiao et al. [28] and Tao et al. [29] respectively at 180 and 160 °C. Rownaghi et al. [30] using the hydrothermal method with ratio SiO_2/Al_2O_3 = 50 for 24-30 hours at 140-170 °C. Xu et al. [31] was studied the activity of hierarchical ZSM5 synthesized at 100 °C for 8-36 hours for the crystallization time variation of phenol alkylation reaction. Qoniah [32] has developed hierarchical synthesis of ZSM-5 from kaolin as a source of silica and alumina, silicalite seed is added as to induced of ZSM-5 structure and CTABr for meso structure. Hierarchical ZSM-5 synthesized with temperature aging at room temperature for 12 hours. Crystallization temperature at 80; 127.5 and 175 °C, and each time the crystallization temperature variation of crystallization is carried out for 12, 24 and 48 hours. The results showed that the samples with a crystallization for 24 hours at temperature 127.5 °C began to show the formation of ZSM-5 and has wide surface area and mesoporous high enough. So, in this paper we will describe the influence of crystallisation stage on the formation of mesoporous ZSM-5 in the presence cationic surfactant cetyltrimethylammonium bromide.

RESEARCH METHOD

1. Synthesis of Mesoporous ZSM-5

The mesoporous ZSM-5 were prepared by a one-step crystallization. The respective seeding gels with a molar composition of: 10 Na_2O : 100 SiO_2 : 2 Al_2O_3 : 1800 H_2O, were prepared by dissolving natrium hidroxide in solution of H_2O. After its complete dissolution, kaolin (Bangka Belitung) as silica and alumina source was added to the mixture and

homogenized by stirring. The mixture was stirred for 30 min. Then Ludox or Colloidal Silica (Aldrich, SiO_2 30%) and remaining of H_2O was added drop wise, the resulting mixture was stirred for 8 h at room temperature. The mixture was aged at room temperature for 12 h. Then silicalit seed (1 % mass of solid) was added to the mixture and stirred for 30 min. The new mixture was transferred an into autoclave for further hydrothermal treatment and at crystallization 127.5 °C for 24 h. After crystallization, cetyltrimethylammonium bromide (CTABr) was added (SiO_2/CTAB = 3.85) and the mixture stirred until its complete dissolution. This final mixture, was further aged for 4 h at room temperature. The resulting solid was filtered, washed with distilled water and dried at 60 °C over night. Finally, The samples were calcined at 550 °C under continuous flow of N_2 for 1 h, followed the powder was calcined in air at 550 °C for 6 h to completely remove the organic surfactants.

Procedures synthesis of mesoporous ZSM-5 with two-step crystallization is almost similar to the above, the difference is only on the step of crystallization. After the mixture was aged at room temperature for 12 h, silicalite seed (1 % mass of solid) was added to the mixture and stirred for 30 min and CTABr was added and crystallized at temperature 150 °C for 24 h to the second crystallization. The next step is same as above procedure. Samples were formed given the symbol ZSM-5 K-1 for sample with one-step crystallization, while ZSM-5 K-2 for sample with two-step crystallization.

2. Characterization

The solids were characterized by X-ray diffraction, FTIR, nitrogen adsorption and SEM-EDX. XRD measurements were carried out using Cu Kα radiation on the Philips Expert diffractometer in the range of 5°-40° (2θ), λ =1.54056 Å for phase identification and determination of the relative crystallinity. The infrared spectra were recorded using the KBr pellets and Shimadzu FTIR Spectrometer in the range between 1400 and 400 cm^{-1}. The nitrogen sorption isotherms were obtained using a Quantachrome Corporation (Nova-1200) instrument. Prior to the analysis, approximately 0.05 g of each sample was treated under vacuum for 3 h at 300 °C. The specific surface area (S_{BET}) was estimated by the BET equation, while the pore size distribution (PSD) and the mesopore analysis were determined from the desorption, as well as, from the adsorption branch of the nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) method. The scanning electron microscopy-EDX (SEM-EDX) micrographs were obtained on a ZEISS EVO MA 10 and EDX BRUKER 129 EV microscope operating.

RESULT AND DISCUSSION

XRD technique is used to identify the crystalline phase, crystal structure and crystallinity of the sample. On the characterization using XRD was observed diffractogram of sample with one-step (ZSM-5 K-1) and two-step crystallization (ZSM-5 K-2). In this research, the XRD analysis using angle (2θ) between 5°-40°. X-ray diffraction pattern of the mesoporous ZSM-5 sample with variation of crystallization stage is shown in Figure. 1. Characteristic diffraction peaks at 2θ of all samples is 7.9°; 8.8°; 23.07°; 23.37° and 23.95°. This is consistent with results reported Treacy and Higgins [33] that the main peak of ZSM-5 with MFI-type zeolite structure at 2θ = 7.8°; 8.8°; 23°; and 23.8°. This indicates that the solid results of the synthesis included in the MFI structure type. The diffractogram pattern shows that the sample of ZSM-5 K-1 form amorphous (resembling mound), while sample of ZSM-5 K-2 was crystalline. It is characterized by relatively high intensity of sample ZSM-5 K-2 when compared to ZSM-5 K-1. Some small peaks were present for the ZSM-5 K-1 sample. Some significant zeolite ZSM-5 peaks were observed at two-step crystallization. ZSM-5 K-1 sample was synthesized using

one-step crystallization lead crystal growth is not perfect because of too rapid crystallization [34]. On the other hand, the nucleation stage at higher temperature leads to accelerated nucleation and this is followed by the crystallization stage at lower temperature for the control of crystallite size [35].

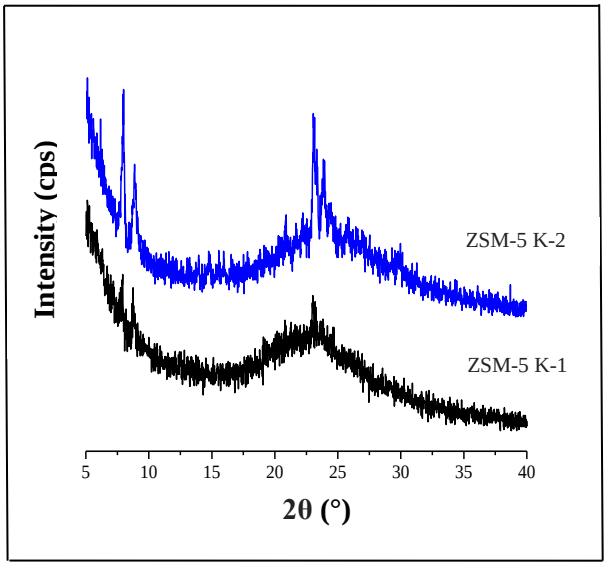

Figure. 1. XRD patterns of the samples.

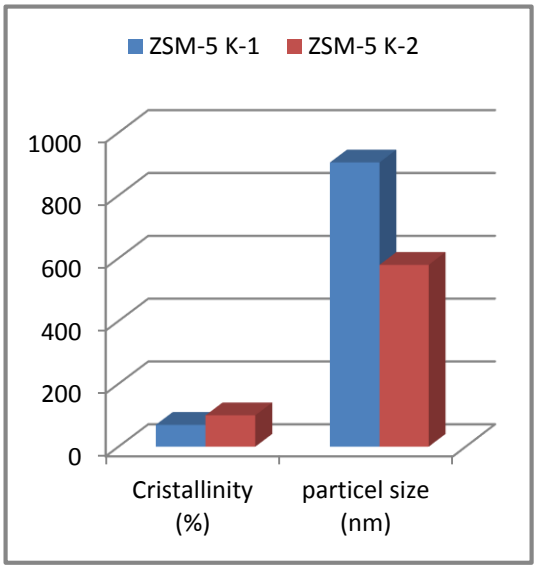

Figure. 2. The relation between crystallinity with particle size of samples.

Therefore, in this study it is clear that the time and temperature of crystallization influences the formation of mesoporous ZSM-5. To compare the intensity and crystallinity of each sample with crystallization stage variation can be seen in Table 4.1. Crystallization time is getting longer and high crystallization temperature causes higher peak intensity. The higher the intensity, the crystallinity of the sample will also be higher. Time on the formation of zeolite crystallization was achieved from solution phase into the gel phase became solid phase. The process occurs continuously beginning with the condensation reaction and followed by a saturated solution polymerization to form a bond of Si-O-Al [36].

The crystallinity of the ZSM-5 K-1 and ZSM-5 K-2 samples were 69.59% and 100%, respectively. Figure 2 describes the relation between crystallinity with particle size (Scherrer equation estimation). The higher crystallinity causes the smaller particle size. The difference in the intensity of the formation of ZSM-5 crystals due to the number of fields generated at each of the different samples, so that the amount of light reflected from crystal planes will also be different. Samples were able to reflect more light will produce a high intensity, so that the crystallinity of ZSM-5 produced will also be higher.

Table 1. The content of phase, intensity, crystallinity and average particle size of the samples

Sample	**Phase**	**Intensity (cps)**					**% Relative cristallinity[a]**	**Particle Size[b] (nm)**
		7.9°	**8.8°**	**23.07°**	**23.37°**	**23.95°**		
ZSM-5 K-1	Amorf and ZSM-5	317	293	262	233	220	69.59	905
ZSM-5 K-2	ZSM-5	456	331	422	358	337	100	579

[a] crystallinity was calculated from the amount of highest peak intensity of the sample compared to the amount of highest peak intensity standard

[b] calculation of particle size using Scherrer equation [37]

Results obtained by XRD were confirmed with those of SEM. This technique was used to determine the morphology and the particle size. Fig. 3 compares the SEM-EDX images of the ZSM-5 K-1 and ZSM-5 K-2 samples. Images of ZSM-5 K-2 sample consist of small crystals, ca. 1000 nm. However, decreasing the crystallization temperature from 150 to 127.5 °C was resulted large crystals zeolite appeared with a size more that 1 μm, embedded in amorphous aggregates. Therefore, the crystallization temperature should be as low as possible to obtain small crystals. Its boundary between the particles could not be clearly observed by SEM. For the samples of ZSM-5 K-1 and ZSM-5 K-2, the crystallite size from SEM analysis was about 1.0 -2.0 μm while the crystallite size was about 1.0 μm, respectively. EDX spectrum results show that the samples composed of elements - elements that are used as precursors, namely Na, Si, Al and O. This indicates that there are no other elements that are formed during the synthesis process. In addition, not found any other elements that indicate the absence of impurities in the samples synthesis results.

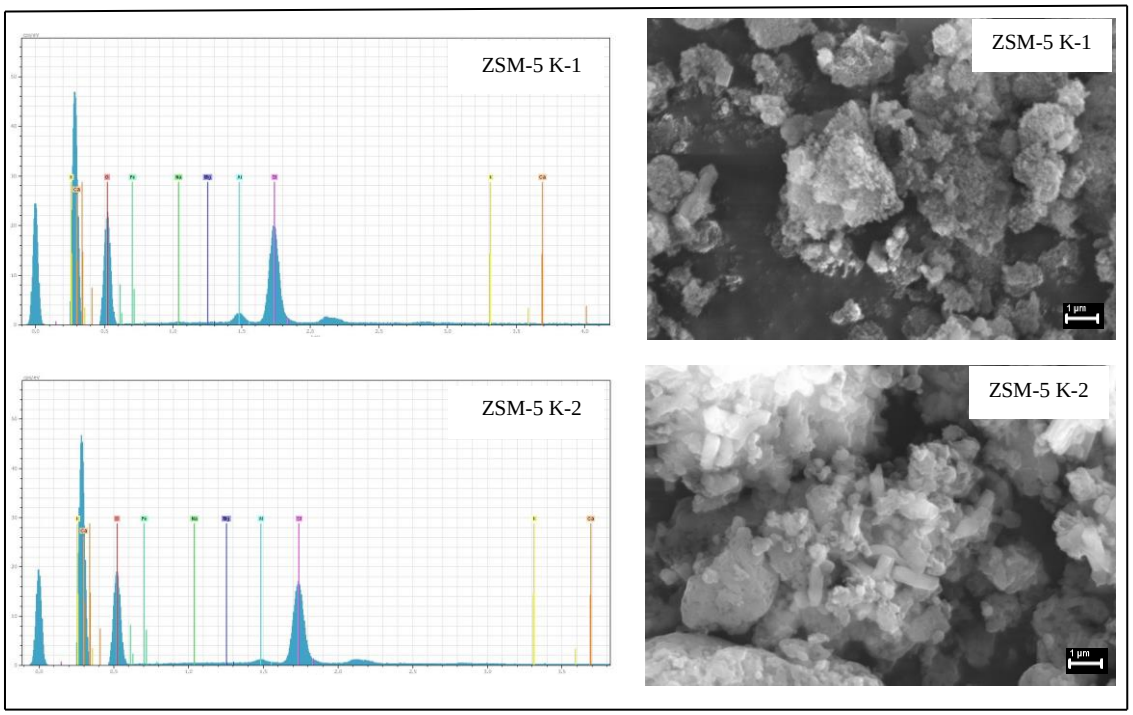

Figure. 3. SEM-EDX images of the samples prepared under different crystallization step

The FTIR spectra of the ZSM-5 K-1 and ZSM-5 K-2 samples between 400 and 1400 cm^{-1} are shown in Figure 4. Furthermore, FTIR pattern shows us the absorption bands at 1226, 1087, 794, 551 and 459 cm^{-1}. Absorption band at wave number that is characteristic to the formation of ZSM-5. The Absorbtion bands about 1226 cm^{-1} is atrributed external asymmetric strecth vibration. The Absorbtion bands about 459 cm^{-1} is atrributed to structure insensitive internal tetrahedron vibrations (T–O bend), 794 cm^{-1} is attributed to structure insensitive internal tetrahedron or structure sensitive external tetrahedron (external symmetric stretch) were typical for highly siliceous materials [38]. The shoulder observed at 960 cm^{-1} indicates the presence of terminal silanol groups on the surface of the mesopore walls [25]. A structure sensitive band, which appears in the spectra about 551 cm^{-1} , indicates the presence of typical

five ring units of the ZSM-5 structure and characteristic structure of MFI-type zeolites [25]. The broad bands about 1226 cm^{-1} are showed at ZSM-5 K-1 sample. Relatively small absorbtion band is also shown in the wave number about 551 cm^{-1} for ZSM-5 K-1 sample. This shows that the sample with one-step crystallization yet perfectly formed ZSM-5 crystal. Both the XRD and the IR pattern can indicate that MFI-type zeolite has been successfully synthesized for ZSM-5 K-2 sample.

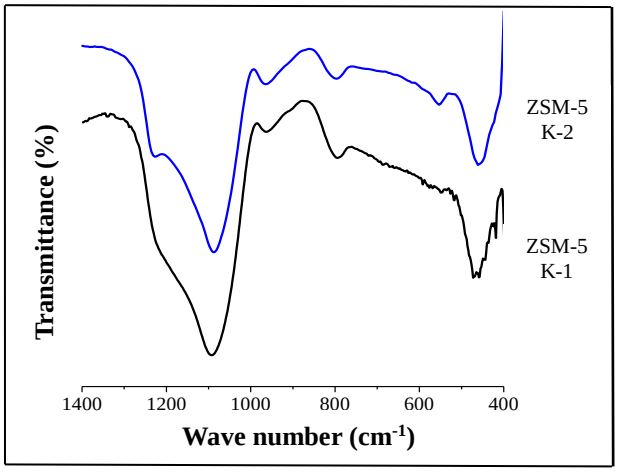

Figure 4. FTIR spectra of samples

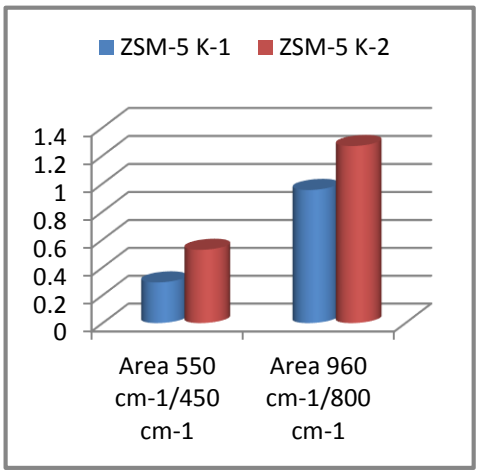

Figure. 5. Chart area ratio of 550 cm^{-1}/450 cm^{-1} and 910 cm^{-1}/800 cm^{-1}

Frequently the ratio between the area of the structure sensitive band about 550 cm^{-1}, attributed to the five-rings of the pentasil structure and the area of the structure insensitive band about 450 cm^{-1}, attributed to internal tetrahedron vibrations, is taken as a measure for the crystallinity of the ZSM-5 zeolites [39,40]. It can be seen from Fig. 5, that ZSM-5 K-2 has a higher crystallinity compared to ZSM-5 K-1, the result is consistent with the characterization using XRD which showed that the ZSM-5 K-2 has a higher crystallinity. While the ratio of 960 cm^{-1} /800 cm^{-1} area indicates the area mesoporous characterized by vibration of Si-OH. From Fig.5 shows that the sample of ZSM-5 K-2 has a fairly high amount of mesoporous compared to ZSM-5 K-1.

The isotherms of the nitrogen adsorption-desorption of mesoporous samples are shown in Fig. 6, and mesoporous area, pore diameter and mesoporous volume are demonstrated in Table 2. The N_2 adsorption-desorption data of the mesoporous ZSM-5 presented in Table 2 indicate the presence of mesopores. Correspondingly, the pore size gives a diameter at about 6.36 nm and 2.83 nm for ZSM-5 K-1 and ZSM-5 K-2, respectively. This indicates that ZSM-5 obtained in this work has indeed a meso structure. It is believed that the preparation of synthesis mixture and hydrothermal reaction conditions are key factors influencing crystal morphology, porosity and crystal size. Since inter-crystalline porosity is developed, this simple method opens novel avenues for catalyst design by improved diffusion characteristics.

Table 2. Textural properties of mesoporous ZSM-5

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	Pore Diameter (nm)	Mesoporous volume (cm^3/g)
ZSM-5 K-1	670.48	325	6.36	0.515
ZSM-5 K-2	779.89	882	2.83	0.625

The N_2 adsorption-desorption isotherms for some samples are typical type IV sorption

isotherms (Fig. 6). These isotherms show hysteresis loops in the $P/P_0 > 0.9$ for ZSM-5 K-1, and $P/P_0 > 0.35$ for ZSM-5 K-2 which are characteristic of mesoporous materials. However, the isotherm of the samples is different. these isotherms indicate that there are obvious mesopores in the composite molecular sieves, and the mesoporous structure strongly depended on the heat treatment conditions. The presence of pores on the surface of the solids will give the effect of limiting the amount of layers in the adsorbate and capillary condensation phenomenon. The capillary condensation causes hysteresis [41]. Hysteresis occurs due to the relative pressure P/P_0 is the same, the amount of nitrogen molecule is desorp shows the difference (less) than the number of nitrogen molecules adsorbed [42].

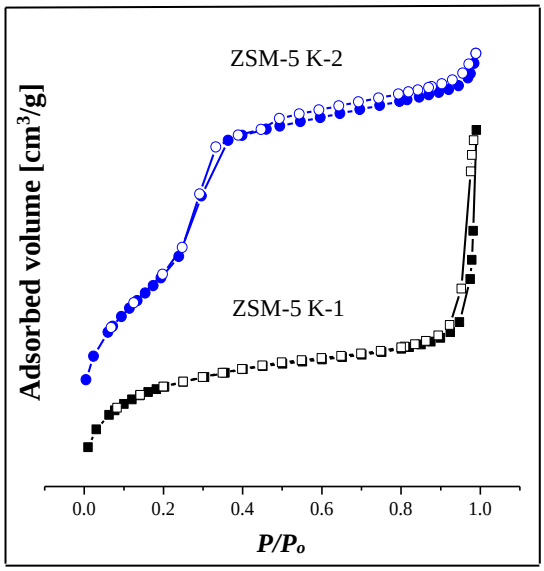

Figure. 6. N_2 adsorption-desorption Isotherms of samples

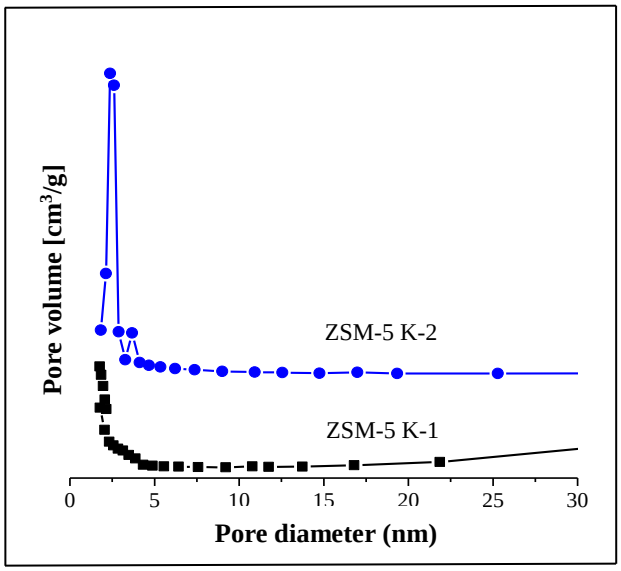

Figure. 7. Pore size distribution of samples obtained by the BJH method

Fig. 7 shows the pore size distribution of sample determined by the BJH method from the adsorption branch of the nitrogen isotherms, which reveal for samples mean pore diameters near to 3 nm. In Fig. 7 shows that the ZSM-5 K-2 sample, the intensity of which is showed in the picture the higher than ZSM-5 K-1 sample, and there is pore diameter between 2-5 nm. At a pore diameter about 2-5 nm showed an increase in intensity with two-step crystallization. Based on Fig. 7 it can be concluded that the presence of hysteresis on ZSM-5 samples due to the meso-sized pores.

CONCLUSION AND SUGGESTION

Mesoporous ZSM-5 has been successfully synthesized from gel synthesis of ZSM-5 using one-step and two-step crystallization in the presence of cationic surfactants CTABr. Mesoporous ZSM-5 small particle aggregates were synthesized in the two-step crystallization by controlling the crystallization time and temperature. The specific mesoporous area was increased as the particle size decreased. Characterization using XRD results showed that the higher the temperature crystallization causes crystallinity of the sample will increase. Nitrogen adsorption-desorption results showed that the mesoporous ZSM-5 with two-step crystallization has mesoporous area is equal 882 m^2/gr, higher than mesoporous ZSM-5 with one-step crystallization.

Advice on this research needs to be done to the application of mesoporous ZSM-5, so it can be learned catalytic activity.

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